

PATENT SPECIFICATION

(11) 1 466 064

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(21) Application No. 10890/73 (22) Filed 6 March 1973

(23) Complete Specification filed 6 March 1974

(44) Complete Specification published 2 March 1977

(51) INT CL³ C08F 2/20 12/08 20/00

(52) Index at acceptance

C3P 102 7D2A1 7K8 8D1B 8D2A 8D2B2 8D4 8K7 8K8 D7
PIC P1E5 P1F P2A1 P2A4 P4A P6A

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(54) PRODUCTION OF EMULSION POLYMERS

(71) We, JAMES FERGUSON & SONS LIMITED, a British Company of Lea Park Works, Prince Georges Road, Merton Abbey, London SW19, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with improvements in or relating to emulsion polymers.

Emulsion polymers prepared in aqueous media are widely used in the surface coatings industry and have been traditionally of two types known as "colloid based" and "non-colloid".

"Colloid based" emulsion polymers may be prepared by the emulsion polymerisation of vinyl acetate monomer in the presence of an initiator. Such polymers may be modified to enable them to form a film at low temperatures by the addition of an external plasticiser such as dibutyl phthalate, or by copolymerising with a "soft" monomer such as an alkyl ester of acrylic or maleic acids, the vinyl ester of an organic acid such as Versatic acid or capric acid, or with ethylene (Versatic is a Registered Trade Mark).

Such emulsions may be prepared by heating and stirring a solution in water of a colloid such as hydroxyethyl cellulose or polyvinyl alcohol to 65—95°C and adding continuously over a period of 2½—5 hours a steady stream of the monomer or monomer mixture.

An initiator such as an unstable peroxide or per-salt is usually present to generate a steady stream of free radicals which initiate the reaction. Other agents may also be added, for example, buffers to control the pH, and anionic and non-ionic surfactants which

imparted with advantage to the composition by the addition of certain special synthetic or modified clays such as Bentonite and the material known commercially as "Laponite" (Laporte Industries Ltd.). Laponite is a Registered Trade Mark. One may also use titanium complexes such as di- and tri-ethanolamine titanates and the commercial products Tilcom AT1, AT2, AT3, ATL1, ATL2, and ATL3 (Titanium Intermediates Ltd. (Tilcom is a Registered Trade Mark) and Zirconium complexes e.g. Zircomplex P (Hardman & Holden Ltd., Zircomplex is a Registered Trade Mark). A gel structure is formed which can be broken under the influence of high shear (for example when a paint is brushed).

The choice of monomers that have been usually employed in non-colloid emulsions is greater than in colloid based emulsions; however non-colloid emulsions have not been found to have satisfactory gelling characteristics for use in the preparation of thixotropic paints. Premature coagulation of the polymer frequently occurs in the preparation of emulsion polymers based on olefinically unsaturated monomers other than vinyl acetate in aqueous media in the presence of a colloid particularly cellulose derived colloids such as hydroxyethyl cellulose. It is often desirable to prepare colloid based emulsion polymers containing or consisting of monomers other than vinyl acetate (particularly the class of emulsion polymers known generically as "acrylics") to satisfy performance criteria placed upon the polymer. The problem of premature coagulation may preclude the preparation of such polymers at the desired solids content. However by analogy with colloid-based vinyl acetate copolymers such colloid-based acrylics should be expected to exhibit improved flow and

SPECIFICATION NO 1466064

By a further direction given under Section 17 (1) of the Patents Act 1949 this application proceeded in the name of REED INTERNATIONAL LIMITED, a British Company, of 82 Piccadilly, London W1A 1EJ.

THE PATENT OFFICE

Bas 34523/5 170

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An initiator such as an unstable peroxide or per-salt is usually present to generate a steady stream of free radicals which initiate the reaction. Other agents may also be added, for example, buffers to control the pH, and anionic and non-ionic surfactants which modify the particle size and aid stability.

Colloid based emulsion polymers may, with advantage be used in the production of thixotropic compositions useful for applications such as paints, adhesives and surface coatings. Conveniently thixotropy may be

imparted with advantage to the composition by the addition of certain special synthetic or modified clays such as Bentonite and the material known commercially as "Laponite" (Laporte Industries Ltd.). Laponite is a Registered Trade Mark. One may also use titanium complexes such as di- and tri-ethanolamine titanates and the commercial products Tilcom AT1, AT2, AT3, ATL1, ATL2, and ATL3 (Titanium Intermediates Ltd. (Tilcom is a Registered Trade Mark) and Zirconium complexes e.g. Zircomplex P (Hardman & Holden Ltd., Zircomplex is a Registered Trade Mark). A gel structure is formed which can be broken under the influence of high shear (for example when a paint is brushed).

The choice of monomers that have been usually employed in non-colloid emulsions is greater than in colloid based emulsions; however non-colloid emulsions have not been found to have satisfactory gelling characteristics for use in the preparation of thixotropic paints. Premature coagulation of the polymer frequently occurs in the preparation of emulsion polymers based on olefinically unsaturated monomers other than vinyl acetate in aqueous media in the presence of a colloid particularly cellulose derived colloids such as hydroxyethyl cellulose. It is often desirable to prepare colloid based emulsion polymers containing or consisting of monomers other than vinyl acetate (particularly the class of emulsion polymers known generically as "acrylics") to satisfy performance criteria placed upon the polymer. The problem of premature coagulation may preclude the preparation of such polymers at the desired solids content. However by analogy with colloid-based vinyl acetate copolymers such colloid-based acrylics should be expected to exhibit improved flow and opacity in emulsion paints and improved resistance to alkali in all applications. Heretofore it has not proved possible using products from the prior emulsion formulation art to formulate satisfactory water-based paints exhibiting sufficient thixotropy to give

a truly "non-drip" property without deterioration of other important paint properties on emulsion polymers containing a major proportion of the alkyl esters of acrylic and methacrylic acids and styrene.

We have now found a method of preparing such emulsion polymers in aqueous media in the presence of a colloid, e.g. hydroxyethyl cellulose, which method does not give rise to coagulation during the preparation of the emulsion and which method may be particularly applied to styrene or monomers derived from acrylic or methacrylic acid. It is believed that coagulation of such polymers previously occurred due to either interaction or grafting occurring during the polymerisation reaction between the colloid and the growing polymer chains, resulting in the formation of grit and even possibly total coagulation.

In our method such coagulation is prevented and grit substantially reduced by effecting the emulsion polymerisation in the presence of a low molecular weight cellulosic colloidal material or a low molecular weight material obtained by degradation of a cellulosic colloidal material (both materials being referred to herein as "low molecular weight cellulosic material"). The low molecular weight colloidal material may be derived by partially degrading the colloid by means of a per-salt or other suitable reagent. Apart from the inclusion of the low molecular weight cellulosic material the polymerisation is otherwise effected in the usual way. It is believed that the degraded colloid is less able to bridge the inter-particle distances within the emulsion. The polymerisation is preferably effected in the presence of a chain transfer agent since such agents appear to hinder grafting occurring between the polymer and the colloid.

According to the invention there is provided a process for the preparation of a colloid based emulsion polymer which comprises polymerising an aqueous emulsion of an olefinically unsaturated monomer or mixture of monomers comprising at least 80% by weight of acrylic monomers and/or styrene in the presence of an initiator, a dispersing agent and a low molecular weight cellulosic material or a partially degraded cellulosic colloidal material, the said low molecular weight cellulosic material or partially degraded cellulosic colloidal material having a viscosity of up to 50 cps as measured on a 5% aqueous solution of the material in an Epprecht viscometer (Cup A speed III). The process is preferably carried out in the presence of a chain transfer agent.

The partially degraded colloid may conveniently be prepared in an initial reaction prior to the emulsion polymerisation. Thus a conventional high molecular weight colloid may be partially degraded prior to the poly-

merisation reaction by heating, for example, with a peroxide e.g. *t*-butyl hydroperoxide, a salt of a per acid e.g. ammonium persulphate or by treating the high molecular weight colloid with an enzyme such as cellulase. Suitable colloids include hydroxyethyl cellulose or carboxymethylated hydroxyethyl cellulose. Particularly advantageous gelling characteristics of the resulting polymer occur when the colloid used is partially degraded hydroxyethyl cellulose.

The low molecular weight cellulosic material may be used in amounts of from 0.01 to 10% by weight, preferably from 0.05 to 2% by weight, based on the weight of the monomers.

The degradation of the colloid may readily be achieved by heating in the presence of the peroxide or the salt of the per acid. Heating for 10 to 60 minutes, preferably from 20 to 40 minutes, at 70–90°C has proved to be satisfactory. Longer periods of heating are required to achieve the desired degree of degradation at lower temperatures while correspondingly shorter periods are required at higher temperatures. Degradation may be efficiently achieved with at least 1% and preferably 5–30% by weight of the peroxide or per acid salt based on the weight of the high molecular weight colloid.

Colloids having a viscosity of up to 50 cps as measured on a 5% aqueous solution of the material in an Epprecht viscometer (Cup A speed III) yield satisfactory results however the preferred viscosity range is from 5 to 25 cps. Such viscosities may, in general, be achieved by degrading colloids in the manner described above with from 0.1 to 10% by weight of ammonium persulphate.

The process according to the invention may, with advantage, be effected in the presence of a chain transfer agent and suitable chain transfer agents include sulphur containing compounds such as long chain alkyl mercaptans for example *n*-dodecyl mercaptan, and thioglycollates such as ethylene bis thioglycollate. Other suitable chain transfer agents are halogenated materials of the type known in the art. The chain transfer agent may be used in amounts of 0.01 to 10% by weight, preferably from 0.5 to 2% by weight based on the weight of monomers.

Emulsion polymers having a solids content of 30–60% by weight may readily be prepared by the methods according to our invention.

The emulsion polymerisation may be carried out in the presence of a dispersing agent which may be of the anionic, cationic or nonionic type.

Suitable anionic dispersing agents include alkali metal salts of sulphuric, sulphonic or sulposuccinic acids containing e.g. long hydrocarbon chains for example the sodium

salts of dioctylsulphosuccinic acid or lauryl sulphuric acid or alkarylsulphonic acids e.g. sodium dodecyl benzene sulphonate. Other anionic dispersing agents that may be used are sulphated derivatives of ethoxylated lauryl alcohol or a corresponding acid; sulphated derivatives of ethoxylated alkyl phenols or cresols; half esters and salts of mono- or dialkyl sulphosuccinic acids and ethoxylated derivatives thereof such as ethoxylated half esters of sulphosuccinic acids; alkali metal, amine or ammonium salts of sulphated or sulphonated alkyl or alkaryl ethoxylates; salts of sulphated unsaturated esters such as the sodium salt of sulphated butyl oleate; and phosphoric acid esters e.g. an alkyl phenoxy poly(oxyethylene)ethyl ester of phosphoric acid. The nonionic dispersing agents are conveniently the polyoxyethylene derivatives of various hydrophobic organic molecules, for example such derivatives of nonyl phenol, straight or branched chain alkyl alcohols or acids or sorbitan fatty acid esters. Other suitable non-ionic dispersing agents are polyoxyalkylenes e.g. block copolymers comprising blocks of polyoxyethylene and polyoxypropylene units. The dispersing agent may be used in amounts of up to 10 per cent preferably from 1 to 4 per cent by weight based on the total weight of the monomers.

Examples of suitable acrylic monomers are esters of acrylic or methacrylic acid with alkanols containing 1—22 e.g. 1—4 carbon atoms or the free acids themselves. Advantageous results may be obtained when the acrylic monomer is ethyl acrylate, methyl methacrylate or butyl acrylate.

These monomers may be copolymerised with not more than 20% by weight, of another olefinically unsaturated monomer. Examples of such co-monomers include esters of ethylenically unsaturated acids such as itaconic, crotonic or maleic acid with alkanols containing 1—22, e.g. 1—4 carbon atoms or the free acids themselves; vinyl chloride; vinylidene chloride; acrylonitrile; acrylamide; methacrylonitrile; methacrylamide; N-methylol acrylamide; diacetone acrylamide; vinyl or allyl esters of saturated fatty acids containing 3—12 carbon atoms and ethylene and homologous α -olefins containing 3—22 carbon atoms.

The emulsions may be prepared by any convenient emulsion polymerisation technique including batch, semi-continuous and continuous processes in the presence of an initiator for example a peroxide or a salt of a per-acid, e.g. ammonium persulphate that is subject to decomposition at a temperature convenient to the process e.g. 65—95°C. A redox system may also be used as initiator for example a mixture of sulphite and persulphate e.g. in the form of alkali metal salts. Redox reactions are usually

carried out at from 30—70°C. The initiator may be added in small amounts e.g. up to 2% based on the total weight of the monomers and may be present in totality at the beginning of the reaction or a part thereof may be added continuously or intermittently during the course of the reaction.

In order that the invention may be well understood the following Examples are given by way of illustration only. The words Natrosol, Cellosize and Veova as used hereinbelow are Registered Trade Marks. All parts, percentages and ratios are, unless otherwise stated, by weight.

Example 1

The following mixtures were prepared:

	parts	
A {	Hydroxyethyl cellulose (1)	5.0
	Ammonium persulphate	0.5
	t-butyl hydroperoxide	0.5
	water	320.0
B {	Methyl methacrylate	210.0
	Butyl acrylate	210.0
	Sulphated octyl cresol 8.5 moles ethylene oxide adduct,	
	sodium salt (30% solution)	40.0
	Water	150.0
C {	Ammonium persulphate	1.5
	Water	30.0
D {	Ammonium persulphate	0.5
	Water	5.0

(1) Natrosol 250 LR (Hercules)

Mixture A was loaded into a vessel equipped with a 5 way lid through which passed a stainless steel stirrer, a thermometer, a reflux condenser, a nitrogen inlet and a dropping funnel for the slow addition of reactants, and heated at 80°C for 30 minutes. This stage converted the colloid to partially degraded colloid. After cooling slightly 15 parts of B and 10 parts of C were added. After 10 minutes at 80°C balance of B and C was added over 3 hours. D was added and the emulsion was held at 80—85°C for 30 minutes before cooling, and the pH adjusted to 9 with ammonia. A stable emulsion was produced which was found to be essentially free of grit and unpolymerised monomer. Its particle size was 310 nm by light scattering and its viscosity was 1.3 poise and the emulsion gelled firmly on addition of Diethanolamine titanate, Tilcom AT1, Tilcom AT2 or Tilcom ATL2. A weaker gel was produced by triethanolamine titanate and Zircomplex P.

Example 2

This example was similar to Example 1

except that reactive monomers methacrylic acid (5 parts) and acrylamide (5 parts) were added to monomer pre-emulsion 'B'. An emulsion possessing similar characteristics to that prepared in Example 1 was obtained. The emulsion gelled on addition of the previously used range of titanium and zirconium complexes.

Example 3

This example was similar to Example 1 except in mixture A 0.75 parts ammonium persulphate were used in place of the previous ammonium persulphate t-butyl hydroperoxide mixture. An emulsion possessing similar characteristics to that prepared in Example 1 was obtained. The emulsion gelled on addition of the previously used range of titanium and zirconium complexes.

Example 4

This example was similar to Example 3 except that the level of ammonium persulphate was reduced to 0.5 parts. An emulsion possessing similar characteristics to that prepared in Example 1 was obtained. The emulsion gelled on addition of the previously used range of titanium and zirconium complexes.

Example 5

This example was similar to Example 1 except that 0.25 parts ammonium persulphate and 0.75 parts t-butyl hydroperoxide were used in the initial degradation reaction. The initial degradation reaction was effected for 30 minutes at 90°C. An emulsion having a viscosity of 3 poise and possessing similar characteristics to that prepared in Example 1 was obtained. The emulsion gelled on addition of the previously used range of titanium and zirconium complexes.

Example 6

This example was similar to Example 4 except that Natrosol 250 GR replaced Natrosol 250 LR as the hydroxyethyl cellulose in mixture A. An emulsion possessing similar characteristics to that prepared in Example 1 was obtained. The emulsion gelled on addition of the previously used range of titanium and zirconium complexes.

Example 7

This example was similar to Example 5 except that after initial degradation step a reaction temperature of 65°C was used for the polymerisation reaction and twin streams of ammonium persulphate and sodium metabisulphite were used for initiation. The emulsion made well to give a low viscosity product of about 1 poise and gelled on addition of the previously used range of titanium and zirconium complexes.

Example 8

This example was similar to Example 5 except that the Natrosol 250 LR, the ammonium persulphate and the t-butyl hydroperoxide were all reduced to half. The emulsion made to give a very low viscosity product of about 0.5 poise and although showing a marked gel it was less than with the emulsion of Example 5.

Example 9

This example was similar to Example 5 except that a monomer mixture of methyl methacrylate: 2-ethylhexyl acrylate: methacrylic acid: acrylamide=230:190:5:5 replaced the previously used methyl methacrylate: butyl acrylate: 210:210. An emulsion possessing similar characteristics to that prepared in Example 1 was obtained.

Example 10

This example was similar to Example 5 except that styrene replaced methyl methacrylate. An emulsion possessing similar characteristics to that prepared in Example 1 was obtained.

Example 11

This example was similar to Example 5 except that carboxymethylated hydroxyethyl cellulose replaced hydroxyethyl cellulose. An emulsion possessing similar characteristics to that prepared in Example 1 was obtained. The emulsion gelled on addition of the titanium complexes of the previously mentioned type.

Example 12

The following mixtures were prepared:

	parts	
A	Hydroxyethyl cellulose (1)	25.00
	Ammonium persulphate	1.25
	t-butyl hydroperoxide	3.75
	Water	1590.00
B	Methyl methacrylate	1155.00
	Butyl acrylate	945.00
	Acrylamide	7.50
	Methacrylic acid	5.00
	Sulphated octyl cresol 8.5 moles ethylene oxide adduct	105
	sodium salt 30% solution	175.00
C	Water	750.00
	n-dodecyl mercaptan	10.00
D	Ammonium persulphate	7.50
	Water	150.00
E	Ammonium persulphate	2.50
	Water	25.00

Mixture A was heated to 90°C and maintained at this temperature for 45 minutes. 75 mls of mixture B was added and thereafter processing was effected generally as

described in Example 1. The emulsion obtained had a viscosity of 2.5 poise and gelled on the addition of diethanolamine titanate, Tilcom AT1, Tilcom AT2, Tilcom ATL2 and Zircomplex P.

Example 13

This example illustrates the use of a commercially available low molecular weight hydroxyethyl cellulose "Cellosize WPO2", where degradation is not necessary.

	parts	
A { Hydroxyethyl cellulose	5.00	
Water	310.00	
B { Methyl Methacrylate	210.00	
Butyl Acrylate	210.00	
Sulphated octyl cresol 8.5 moles ethylene oxide Adduct Sodium Salt 30% solution	40.00	
Water	150.00	
C { Ammonium persulphate	1.50	
Water	30.00	
D { Ammonium persulphate	0.50	
Water	5.00	

'A' was heated with stirring and on dissolution 15 mls of mixture 'B' was added with one third of mixture 'C' at 80°C and maintained thus for 10 minutes. The balance of 'B' and 'C' was added over 3 hours, followed by the addition of 'D'. The emulsion was held at 80—85°C for 30 minutes before cooling and the pH adjusted to 9.0 with ammonia. The resultant emulsion had a viscosity of 2.0 poise and gelled on addition of the previously used range of titanium and zirconium complexes.

Example 14

This example illustrates the use of an emulsion prepared by the process according to the invention in the preparation of a paint. An emulsion was prepared as in Example 12 except that components 'A' were as follows:

	parts
A { Hydroxyethyl cellulose (1)	25.00
Ammonium persulphate	2.50
Water	1590.00

Similar results to Example 12 were obtained:

This emulsion was compounded as follows:

	Parts by weight
Mill Base	858
Water	138
Coalescing solvent	24
Defoamer	

	Parts by Weight
Mill Base	
Sodium salt of a polyelectrolyte, 25% aq. solution	96
Titanium Dioxide	1848
China clay	360
Ammonia (s. gr. 0.880)	12
Formalin (40%)	6

Disperse for 5 minutes at 2000 r.p.m. on high speed mixer to Hegman reading 7+

	Parts by weight
Paint Formulation	
Mill Base (prepared as above)	139 139
Emulsion (from Example 12)	154 154
Propylene glycol	14 14
Water	9 —
Alkanolamine titanate	1 —
Synthetic clay gelling agent, 10% aqueous solution	— 10

Note:

- 1) Adjust paint to pH 9.0—9.5 with 0.880 Ammonia before addition of thixotrope (alkanolamine titanate or synthetic clay gelling agent)
- 2) Add thixotrope whilst paint is stirring, then stir for further 5 minutes.

Specification:

P.V.C.=30%
solids =50%

Properties of the paint

1. Gel strength was evaluated after 24 hours on an I.C.I. Rotathinner Gel Strength Tester; The paint gelled with alkanolamine titanate had a gel strength of 180 g.cm⁻²; the paint gelled with synthetic clay had a gel strength of 115 g.cm⁻².

2. Both the paint geled with alkanolamine titanate and the paint gelled with synthetic clay had good gloss and hiding power when brushed out and allowed to dry. Furthermore, both paints had satisfactory flow characteristics.

Example 15

This example shows the application of the invention to wood adhesives.

Emulsion based wood adhesives are usually thickened to a viscosity of 25—100 poise. This is partly to prevent excess adhesive running down the side of the joints and partly to prevent the adhesive wicking into porous wood and starving the joint of adhesive. Acrylics of the prior art have been far too thin for this use unless thickened by the post addition of a colloid (such as polyvinyl alcohol or hydroxyethyl cellulose) or an acrylic thickener solution.

The use of the emulsion prepared as follows in a gelled state precludes the need

for post added thickeners and their resulting defect of increased water sensitivity.

5	A	Hydroxyethyl cellulose (1)	parts
		Ammonium persulphate	5.0
		Water	0.5
10	B	Methyl methacrylate	320.0
		Butyl acrylate	230.0
		Methacrylate acid	190.0
		Acrylamide	1.0
		n-dodecyl mercaptan	1.5
		Nonylphenol 9 moles	2.0
15	C	Ethylene oxide adduct	5.0
		Water	180.0
		Ammonium persulphate	1.5
	D	Water	30.0
		Ammonium persulphate	0.5
		Water	5.0
	E	37% Formaldehyde	2.0
20	F	0.960 Ammonia	12.0

The procedure and apparatus were generally similar to previous examples.

Mixture 'A' was heated to 90°C with stirring and held 25 minutes before cooling back to 70°C. 15 mls of mixture 'B' was added together with 10 mls of mixture 'C'. After 15 minutes during which time the temperature had been raised to 80° and the initial portion of 'B' had polymerised, the

remainder of 'B' and 'C' were started to be run in concurrently over 2.75 hours. 'D' was then added, the emulsion held at 80—85° for 30 minutes and then cooled below 30°C. The preservative 'E' and the pH control 'F' were then added.

A low viscosity emulsion of about 30 cp resulted, which was however free from grit and coagulate. Its surface tension was 36.2 dynes/cm and its particle size 460 nm.

Bond Strength

This was measured by slicing a sheet of chipboard in half and applying an approximately 0.1 cm coating of acrylic of this invention both ungelled (when it is of similar viscosity to most commercial acrylics) and gelled with diethanolamine titanate to about 40 poise (where it was of similar viscosity to most polyvinyl acetate wood glues). Areas of the join were coated and the adhesive allowed to soak into the chipboard for 5 minutes and 1 minute before the two halves were brought together under light pressure and left for 24 hours to dry. The ungelled acrylic had wicked almost completely into the chipboard after 5 minutes while the gelled samples were apparently unchanged.

Bond strength was assessed by cutting the chipboard into 3.6 cm wide strips at right angles to the glue line. One half was supported and weights hung on the other half at a distance of 7.5 cm for the glue join. Results were somewhat variable, but the average weights that were supported before bond failure were as follows:

	Ungelled acrylic	Gelled acrylic
65	1 minute dry before bonding	1350 g
	5 minutes dry before bonding	1550 g
		1760 g

WHAT WE CLAIM IS:—

1. A process for the preparation of a colloid based emulsion polymer which comprises polymerising an aqueous emulsion of an olefinically unsaturated monomer or mixture of monomers comprising at least 80% by weight of acrylic monomers and/or styrene in the presence of an initiator, a dispersing agent and a low molecular weight cellulosic material or a partially degraded cellulosic colloidal material, the said low molecular weight cellulosic material or partially degraded cellulosic colloidal material having a viscosity of up to 50 cps as measured on a 5% aqueous solution of the material in an Epprecht viscometer (Cup A speed 'III').

2. A process as claimed in claim 1 wherein the partially degraded cellulosic colloidal material is partially degraded hydroxyethyl cellulose or carboxymethylated hydroxyethyl cellulose.

3. A process as claimed in claim 1 or claim

2 wherein the partially degraded cellulosic material is prepared in an initial reaction prior to the emulsion polymerisation.

4. A process as claimed in any of the preceding claims wherein partial degradation of the cellulosic colloidal material is effected by heating the cellulosic colloidal material with a peroxide or a per acid.

5. A process as claimed in any of the preceding claims wherein the viscosity is from 5 to 25 cps as measured on a 5% aqueous solution of the material in an Epprecht viscometer (Cup A Speed III).

6. A process as claimed in any of the preceding claims wherein the low molecular weight cellulosic material or partially degraded cellulosic colloidal material is used in amounts of from 0.01 to 10% by weight based on the weight of the monomers.

7. A process as claimed in claim 6 wherein the low molecular weight cellulosic material or partially degraded cellulosic colloidal material is used in amounts of

from 0.05 to 2% by weight based on the weight of the monomers.

5 8. A process as claimed in any of the preceding claims wherein the polymerisation is effected in the presence of a chain transfer agent.

9. A process as claimed in claim 8 wherein the chain transfer agent is a sulphur containing compound.

10 10. A process as claimed in claim 8 or claim 9 wherein the chain transfer agent is used in amounts of from 0.01 to 10% by weight based on the weight of the monomers.

15 11. A process as claimed in claim 10 wherein the chain transfer agent is used in amounts of from 0.5 to 2% by weight based on the weight of the monomers.

20 12. A process as claimed in any of the preceding claims wherein the polymerisation is effected in the presence of a dispersing

agent of the anionic, cationic or nonionic type.

13. A process as claimed in claim 12 wherein the dispersing agent is used in 25 amounts of up to 10% by weight based on the total weight of the monomers.

14. A process as claimed in claim 1 substantially as described herein.

15. A process as claimed in claim 1 substantially as described herein with reference 30 to the Examples.

16. A colloid based emulsion polymer whenever prepared by a process as claimed 35 in any of the preceding claims.

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